

Hydrodechlorination of alachlor in water using Pd, Ni and Cu catalysts supported on activated carbon

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Abstract

The hydrodechlorination of alachlor with hydrogen in aqueous phase was studied in a trickle bed reactor using different activated carbon-supported catalysts. The reactor was continuously fed with a 50 mg/L solution of alachlor in water and a H₂/N₂ gas stream. The variables studied were space-time (44.8–448.3 kg_{cat} h/mol), H₂:N₂ volumetric ratio in the gas phase (1:1–1:4), temperature (308–373 K) and pressure (0.24–0.6 MPa). The results of the hydrodechlorination experiments were evaluated in terms of alachlor conversion and ecotoxicity of the exit stream. High conversion values and important reductions of ecotoxicity were obtained working under mild conditions of temperature (323–348 K) and pressure (0.24 MPa). Palladium catalysts supported on activated carbon were found as the most active in the hydrodechlorination of alachlor, although copper and nickel catalysts led also to high conversions in the 80–93% range. The hydrodechlorination of alachlor was performed successfully with metal loads between 0.5 and 2.5 wt.% on the catalysts. A significant metal leaching was observed from the nickel and copper catalysts, which negatively affected the ecotoxicity of the final effluents. Oxidative treatment of the activated carbon supports with nitric acid previous to the impregnation with the metal precursor improved the anchorage of the active phase and reduced leaching dramatically. Likewise, the activity was not influenced by the oxidation of the supports and reductions of ecotoxicity by more than 90% were observed.

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1. Introduction

The widespread use of fitosanitary products for agricultural and non-agricultural purposes has resulted in the presence of their residues in both surface and ground waters. Pesticides can reach the aquatic environment through direct run-off from crops, leaching, careless disposal of empty containers, equipment washing, etc. [1]. Due to the variability and multiplicity of origins of this pollution the problem becomes difficult to control. Moreover, the toxicity, stability to natural degradation and persistence in the environment of these compounds have been the causes of much concern to the societies and the regulatory authorities around the world. In this sense, the legislation has been constantly adapted to protect and improve the quality of water resources, and some water-soluble fitosanitary products have been designated as priority pollutants.

Compounds such as alachlor, atrazine, chlorofenvinfos, diuron, isoproturon and pentachlorophenol have been detected in surface and ground waters and have the potential to reach the levels that exceed the health-based standards. Special attention has been paid to alachlor, a chlorinated aniline herbicide of widespread use for pre-emergent weed control in corn, soybeans and peanuts crops. Undesirable side effects such as toxicity and carcinogenicity confer to it the character of hazardous pollutant whose presence in water has to be carefully controlled [2].

A number of processes and technologies are available for the treatment of water-containing fitosanitary products. Physical and physico-chemical techniques (coagulation, adsorption on activated carbon, reverse osmosis, etc.) can be used for the removal of such pollutants. These methods are non-destructive and post-treatment and/or careful disposal of the spent adsorbent or the solid wastes generated become necessary, thus substantially increasing the treatment costs. Biological treatments are adopted in many cases as the best available technology for the elimination of organic pollutants, but they are not appropriate when the wastewaters contain recalcitrant toxic contaminants.

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Implementation of cost-effective technologies is needed for a suitable treatment of ground and surface waters polluted with fitosanitary products. The application of oxidative treatments such as advanced oxidation processes (AOPs) has received a significant attention in the last years, since a number of these techniques ($\text{H}_2\text{O}_2 + \text{UV}$, $\text{O}_3 + \text{UV}$, $\text{H}_2\text{O}_2 + \text{O}_3$, photo-Fenton, $\text{TiO}_2\text{--UV}$, etc.) can convert those compounds to less harmful biodegradable species [3]. Farre et al. [4] studied both homogeneous and heterogeneous photocatalytic ozonation for the degradation of biorecalcitrant fitosanitary products such as alachlor, atrazine, clorofenvinfos, diuron, isoproturon and pentachlorophenol. The best results in terms of TOC reduction and detoxification were obtained by means of photo-Fenton/ O_3 treatment, except in the case of atrazine and alachlor. Some economic studies on the application of AOPs have concluded that the research interest should focus mainly on those techniques that can be driven by solar radiation (wavelength above 300 nm) such as photo-Fenton and heterogeneous catalysis with UV/ TiO_2 [3,5,6]. Thus, Hincapie et al. [7] have studied the degradation of alachlor, atrazine and diuron with $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, $\text{Fe}^{3+}/\text{H}_2\text{O}_2$, TiO_2 and $\text{TiO}_2/\text{Na}_2\text{S}_2\text{O}_8$ treatments driven by solar energy using a compound parabolic collector photoreactor. Photo-Fenton using iron at low concentration was found to be efficient for treating aqueous solutions of these fitosanitary products giving rise to a high TOC reduction. Nevertheless, the neutralization of the treated effluent (pH 3), the cost of hydrogen peroxide and a relatively low reaction rate are some factors that must be carefully analyzed before considering the implementation of this treatment.

An alternative approach for the treatment of chlorinated fitosanitary products is catalytic hydrodechlorination. The catalytic hydrogenolysis of organochlorine compounds is a viable, low cost and environmentally friendly methodology which has been applied to different types of chlorinated compounds such as polychlorinated benzenes, chlorophenols, halogenated hydrocarbons, PCBs, dioxins, etc., leading to their conversion into much less harmful substances [8]. This process shows some advantages with regard to other methods for the elimination of chlorinated organics. It can be adapted to wastewaters with a wide range of concentrations, permits to work at mild conditions (pressure and temperature) and the selectivity towards the different reaction products can be controlled through the selection of an adequate catalyst [9–11].

A number of catalysts have been proposed for liquid-phase hydrodechlorination, being carbon-supported catalysts among the most active. They have some advantages such as the relatively low cost of the supports which have a high surface area, the possibility of easy recovery of the supported metal by simple combustion of the support, and good chemical stability [12]. In the case of metallic active phases supported on activated carbon, the surface chemistry plays an important role on the metal dispersion and the catalytic behavior. The surface chemistry can be modified through thermal and/or oxidative treatments which may lead to an increase in the amount of surface oxygen complexes [13]. The most widely used active phases are noble metals such as palladium, platinum, rhodium

and ruthenium, although transition metals have also received attention due to their lower cost and the resistance to corrosion of Ni-based catalysts [14]. Transition metals catalysts have been mainly used supported on alumina, silica or zeolites for hydrodechlorination reactions [15]. Nevertheless, there is so far a scarce literature on hydrodechlorination with copper and nickel catalysts supported on activated carbon. Previous works in literature [14,16,17] only reported the use of nickel and copper in low proportions in bimetallic catalysts. In this work, we report our results on the hydrodechlorination of alachlor using different carbon-supported copper, nickel and palladium catalysts. The efficiency of this treatment was evaluated not only for the herbicide elimination, but also reduction of ecotoxicity.

2. Experimental

2.1. Preparation and characterization of the catalysts

A 0.5 wt.% commercial palladium on activated carbon (Pd/AC) catalyst supplied by Engelhard and different own-made catalysts prepared by wetness incipient impregnation were tested. The catalyst particle size used in the hydrodechlorination experiments was between 1 and 2 mm. The activated carbons used as supports were supplied by Merck (Mk) and Chemviron (Ch). As active phases were used palladium, copper and nickel with a nominal loading of 0.5, 0.5–5 and 0.5–10 wt. %, respectively. The precursor salts employed were PdCl_2 , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$. Impregnation was followed by drying at room temperature for 2 h and overnight at 333 K. Finally, the catalysts were calcined at 473 K and reduced in H_2 atmosphere at 373 K with a flow rate of 60 N mL/min. In some cases, the activated carbon support was subjected to an oxidative treatment with HNO_3 prior to impregnation. Oxidation was carried out by boiling 1 g of activated carbon in 10 mL of 6 N aqueous HNO_3 solution for 20 min [18]. The nomenclature used for the catalysts is shown in Table 1.

The porous structure of the activated carbons and the catalysts was characterized by N_2 adsorption–desorption at 77 K (Autosorb-1 Quantachrome). The BET equation was used to obtain the surface area and the t -method for the micropore volume. The external or non-micropore surface area was also obtained from the t -method. The difference between the volume of N_2 adsorbed at 0.95 relative pressure (calculated as liquid) and the micropore volume was taken as the mesopore volume. The catalysts were analyzed by X-ray photoelectron spectroscopy (XPS), using a Physical Electronics model 5700 apparatus with a Mg $\text{K}\alpha$ X-ray excitation source (1253.6 eV), to determine palladium, copper and nickel concentration.

2.2. Experimental set-up and procedure

The hydrodechlorination experiments were carried out in a trickle bed reactor (9 mm i.d. stainless steel tube) with concurrent downflow of both phases, liquid and gas (Fig. 1). Mass flow controllers were used to prepare different hydrogen/

Table 1
Nomenclature of the catalysts used in hydrodechlorination experiments

Nomenclature	Active phase	Activated carbon	Nominal load (wt.%)
Eng-Pd	Pd	Engelhard	0.5
Mk-Pd		Merck	0.5
Ch-Pd		Chemviron	0.5
0.5Mk-Ni	Ni	Merck	0.5
2.5Mk-Ni		Merck	2.5
5Mk-Ni		Merck	5
10Mk-Ni		Merck	10
0.5Ch-Ni		Chemviron	0.5
2.5Ch-Ni		Chemviron	2.5
2.5ChN-Ni	Ni	Chemviron (HNO ₃)	2.5
5Ch-Ni		Chemviron	5
10Ch-Ni		Chemviron	10
0.5Mk-Cu	Cu	Merck	0.5
2.5Mk-Cu		Merck	2.5
5Mk-Cu		Merck	5
0.5Ch-Cu		Chemviron	0.5
2.5Ch-Cu		Chemviron	2.5
2.5ChN-Cu		Chemviron (HNO ₃)	2.5
5Ch-Cu	Cu	Chemviron	5

nitrogen mixtures that were continuously fed to the reactor. The gas flow (Q_G) and the H₂:N₂ volumetric ratio ranged between 25 and 100 N mL/min and 1:1–1:4, respectively, allowing to work at different hydrogen to liquid ratios. An aqueous solution of alachlor (50 mg/L) was pumped by means of a chromatographic pump (Gilson 307). The liquid flow was varied between 0.1 and 1 mL/min to operate at different space-time (τ) values in the range of 44.8–448.3 kg_{cat} h/mol. The reactor effluent was cooled to 276 K by means of a Peltier cell and finally the samples were collected. The reaction temperature was measured and controlled by a thermocouple inserted in the center of the catalyst bed. The reaction runs were carried out at temperatures and pressures within the 308–373 K and 0.24–0.6 MPa ranges, respectively. Before each run, the catalyst was saturated for 24 h with the initial alachlor solution to improve wetting and reduce the time required to reach the steady-state.

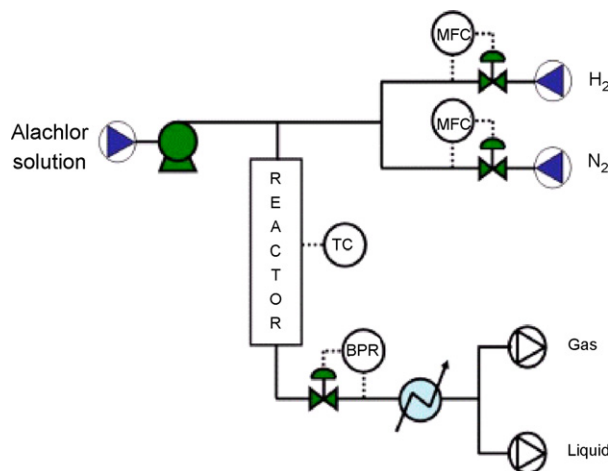


Fig. 1. Scheme of the reaction set-up.

2.3. Analytical methods

The concentration of alachlor was determined by HPLC/DAD (Prostar, Varian) using a C₁₈ column as stationary phase and a mixture of acetonitrile and water (1:1, v/v) at 1.0 mL/min as mobile phase. A wavelength of 220 nm was used for detection. Chloride concentration was determined by means of ion chromatography (Metrohm 790 Personal IC). The ecotoxicity of the liquid samples was determined by means of a bioassay following the standard Microtox test procedure (based on the decreasing of light emission by the marine bacterium *Vibrio fischeri*). A Microtox[®] M500 Analyzer (Azur Environmental) was used. The inhibition of the light emitted by the bacteria was measured after 5 and 15 min of contact time and expressed as ecotoxicity unit (T.U.), which corresponds to the dilution factor that must be applied to the sample in order to obtain a 50% inhibitory effect. The content of copper and nickel in the reactor effluent was determined by colorimetric methods (Orbeco-Hellige 975 MP) according to 308C [19] and 316C [20] standard methods, respectively. Palladium in the reactor effluent was analyzed by total reflection X-ray fluorescence (TRXF), using a TXRF EXTRA II spectrometer.

3. Results and discussion

In a first instance the liquid-phase hydrodechlorination of alachlor was studied with the palladium commercial catalyst. The measured concentrations of Cl[−] ion and the unconverted alachlor in the outlet effluent matched in all the cases the chloride mass balance above 90%. Fig. 2 shows the results obtained at different temperatures and space-time values. The runs performed at 308 K yielded fairly poor results, even at space-times as high as 450 kg_{cat} h/mol. The conversion of alachlor remained around 10% at the most. However, when the reaction temperature was increased up to 323 K, a substantial increase of alachlor conversion was achieved. Beyond this

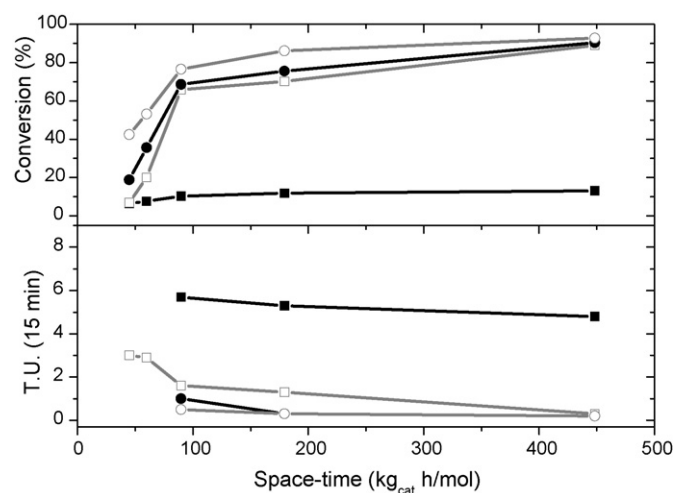


Fig. 2. Influence of temperature and space-time on alachlor conversion and effluent ecotoxicity with the commercial Eng-Pd catalyst: (■) 308 K; (□) 323 K; (●) 348 K; (○) 373 K (P , 0.24 MPa; Q_G , 100 N mL/min; H₂:N₂, 1:1 vol.).

temperature the effect on the activity of the catalyst was markedly less important. Therefore, the use of temperatures above 323 K would not be advisable. In contrast to the trend observed at 308 K, at higher temperatures the conversion of alachlor increased significantly with space-time. A pronounced effect was also observed within the space-time range of 45–180 kg_{cat} h/mol, and no substantial increase of conversion was observed at higher space-time values.

The ecotoxicity of the initial alachlor solution and that of the treated effluents was determined in order to check if the hydrotreatment may lead to the formation of species more toxic than alachlor itself. The ecotoxicity corresponding to a 50 mg/L aqueous solution of alachlor was 6.3 T.U. (15 min). In the runs carried out between 323 and 373 K, the ecotoxicity of the effluent decreased significantly as a result of the hydrodechlorination treatment. As it can be seen, an increase of space-time within the range investigated decreases the ecotoxicity of the final effluent as a consequence of a higher extension of the hydrodechlorination reactions.

Fig. 3 shows the influence of pressure on alachlor conversion. It can be observed that within the pressure range of 0.24–0.6 MPa the conversion remained practically constant. These results are of importance since they reveal that the treatment can be carried out at low pressure, and that under these conditions a convenient hydrogen transfer to the liquid phase is achieved.

The gas flow and the H₂:N₂ volumetric ratio showed a remarkable influence on alachlor conversion (Fig. 4). Thus, when that ratio was maintained at 1:1 and the gas flow reduced from 100 to 50 N mL/min, a drop of 19.2 percentage units was found. Such reduction in gas flow corresponds to a decrease of 50% in the amount of hydrogen fed to the reactor. When a similar reduction in the amount of hydrogen was forced by maintaining the gas flow at 100 N mL/min and reducing the H₂:N₂ volumetric ratio to 1:4 the decrease of conversion was higher (23.8 percentage units). It can also be observed that for a H₂:N₂ volumetric ratio of 1:4 the influence of the gas flow becomes much lower, although it must be indicated that when the gas flow was reduced from 50 to 25 N mL/min, the

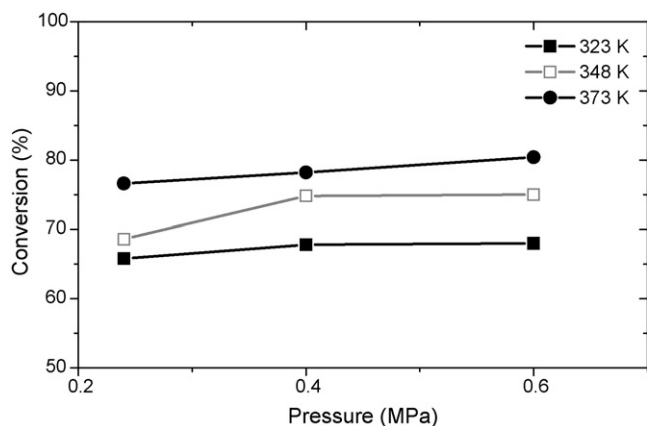


Fig. 3. Influence of reaction pressure on alachlor conversion with the commercial Eng-Pd catalyst (τ , 179 kg_{cat} h/mol; Q_G , 100 N mL/min; H₂:N₂, 1:1 vol.).

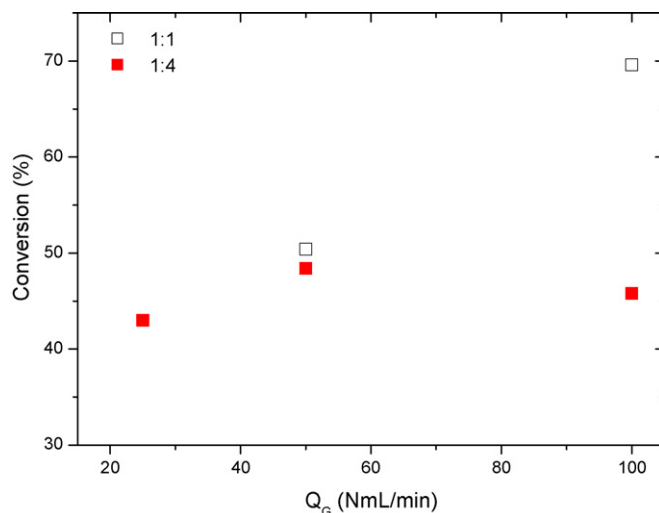


Fig. 4. Influence of gas flow rate and H₂:N₂ volumetric ratio on the hydrodechlorination of alachlor with the commercial Eng-Pd catalyst (T , 348 K; P , 0.24 MPa; τ , 179 kg_{cat} h/mol).

conversion decreased by almost 40%. The stoichiometric flow that would be needed to achieve a complete hydrodechlorination of alachlor would be 6×10^{-4} N mL/min of pure hydrogen. The results discussed above indicate that a large excess of hydrogen is needed to achieve a high alachlor conversion; however, the use of such excess would not be a serious economical drawback, since the gas stream leaving the reactor can be easily recirculated after scrubbing to remove HCl and other possible volatile species.

It is well known that the activity of the activated carbon-supported catalysts is strongly dependent on both the active phase and the properties of activated carbon support [21]. Therefore, some own-made catalysts with different characteristics were prepared, as reported in Table 1. The operating conditions for testing these catalysts were set at 0.24 MPa, 323–348 K, 100 N mL/min, H₂:N₂ (1:1, vol.) and 179 kg_{cat} h/mol space-time. The hydrodechlorination of alachlor was first studied with some own-made catalysts based on palladium, since this metal has been described as the most active in hydrodechlorination reactions [14,22,23]. The results of these experiments are summarized in Table 2, where very high values of alachlor conversion can be observed.

Palladium catalysts on different supports have shown a high hydrodechlorination activity under mild conditions; however, few of them have been introduced to large-scale applications because of the high cost [24]. For this reason, the use of less expensive catalysts based on nickel and copper was also investigated. The nickel catalysts were studied at loads within the 0.5–10 wt.% range, and for the copper catalysts the metal load ranged between 0.5 and 5.0 wt.%, being the results also summarized in Table 2. It can be seen that the catalyst prepared with the Mk activated carbon gave a slightly higher conversion than those made from the Ch one. The copper-based catalysts showed a significantly higher activity than the nickel ones. Conversion values over 92% were achieved for the most active copper catalyst. This is an interesting result since a few studies have been carried out with copper as hydrodechlorination

Table 2

Alachlor conversion with the own-made catalysts based on Pd, Ni and Cu (P , 0.24 MPa; τ , 179 kg_{cat} h/mol; Q_G , 100 N mL/min; $H_2:N_2$, 1:1 vol.)

Catalyst	Conversion (%)	
	323 K	348 K
Mk-Pd	97.5	98.6
Ch-Pd	94.3	96.3
0.5Mk-Ni	82.8	83.9
2.5Mk-Ni	81.6	82.1
5Mk-Ni	79.9	80.4
10Mk-Ni	73.1	76.3
0.5Ch-Ni	78.8	80.2
2.5Ch-Ni	81.6	82.4
5Ch-Ni	76.0	76.8
10Ch-Ni	72.9	73.6
0.5Mk-Cu	92.4	92.9
2.5Mk-Cu	88.7	89.6
5Mk-Cu	88.7	89.7
0.5Ch-Cu	87.6	89.5
2.5Ch-Cu	87.2	89.5
5Ch-Cu	87.4	85.2

catalyst and it has rarely used alone, but together with a noble metal [25–27].

For both nickel and copper series the catalysts with a lower content of metal (0.5–2.5 wt.%) led to the highest alachlor conversion. In order to explain the differences in activity between the catalysts prepared, both the porous structure and the active phase must be considered. The two starting untreated carbons showed some differences in their porous structure, which were analyzed in depth in a previous work [11]. Some of the characteristics of the supports and the catalysts are summarized in Table 3. The BET area and the micropore volume were fairly higher for the Ch carbon while both supports showed comparable values of mesopore volume and external or non-microporous area, which is known to play an important role on the metal dispersion [28]. In general, a high value of BET area with a significant contribution of the area associated to mesopores is consistent with a high availability of easily accessible active sites. Therefore, a higher activity should be expected for the catalysts with such characteristics. However, the conversion results shown in Table 2 do not follow this trend. The highest alachlor conversion for the catalysts prepared with nickel was obtained for the 2.5Ch-Ni, which does not have the largest BET and mesoporous surface area, neither the highest metal load. Thus, it is also necessary to consider the characteristics of the metallic phase. The atomic concentrations

Table 4

Atomic and mass surface concentrations of Ni and Cu of the own-made catalysts as determined by XPS

Catalyst	Ni _{nominal} (wt.%)	Ni _{XPS} (atom.%)	Ni _{XPS} (wt.%)
0.5Ch-Ni	0.5	0.5	2.2
2.5Ch-Ni	2.5	1.1	5.2
5Ch-Ni	5.0	8.9	29.8
10Ch-Ni	10.0	15.6	44.2
Catalyst	Cu _{nominal} (wt.%)	Cu _{XPS} (atom.%)	Cu _{XPS} (wt.%)
0.5Ch-Cu	0.5	0.2	1.1
2.5Ch-Cu	2.5	0.4	1.8
5Ch-Cu	5.0	1.0	4.5

of nickel and copper on the surface, determined by XPS, can be seen in Table 4. A value of the metal concentration measured by XPS significantly higher than the bulk metal concentration indicates that the metallic active phase is deposited mainly on the external surface and suggests a poor distribution, which would result in a lower activity. As can be seen in Table 4, the concentration of the metals on the external surface increased with the nominal bulk metal concentration. Two tendencies can be observed for the nickel catalysts; those with a nominal load between 0.5 and 2.5 wt.% showed low values of the metal concentration on the external surface of the catalyst, whereas for a nickel content higher than 5 wt.% a drastic increase in the concentration of nickel on the external surface was measured. The poor distribution of the metal in the catalysts of higher nominal load would be responsible for the lower conversion values achieved with the 5Ch-Ni and 10Ch-Ni catalysts, in spite of the fact that they have a comparable porous structure.

For the catalysts based on copper, low values of the metal concentration on the external surface were obtained in all the cases, which is indicative of a good distribution of this metal on the support. Very close conversion values were obtained for all the copper catalysts and the activity did not improve with the metal load, probably due to a slight loss of porosity upon impregnation.

One of the drawbacks commonly reported for catalysts based on transition metals is the leaching of the active phase, especially for those reactions carried out in acidic media [29,30]. Therefore, once the good catalytic activity of these catalysts was confirmed, the leaching of metals was studied. Nickel and copper concentrations were determined in the reaction effluent at different times on stream and the results are shown in Fig. 5. Most of the metal leaching took place during

Table 3

Porous structure of the own-made Ch-Cu and Ch-Ni catalysts

Sample	BET area (m ² /g)	External area (m ² /g)	Micropore volume (cm ³ /g)	Mesopore volume (cm ³ /g)
0.5Ch-Ni	710	9	0.329	0.020
2.5Ch-Ni	676	10	0.311	0.020
5Ch-Ni	668	10	0.315	0.023
10Ch-Ni	522	8	0.247	0.019
0.5Ch-Cu	780	11	0.369	0.019
2.5Ch-Cu	713	10	0.331	0.009
5Ch-Cu	582	9	0.271	0.007

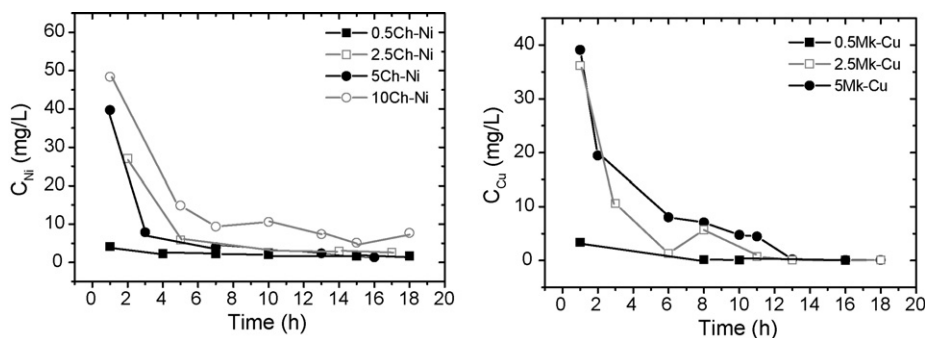


Fig. 5. Evolution of nickel (left) and copper (right) leaching with time-on-stream.

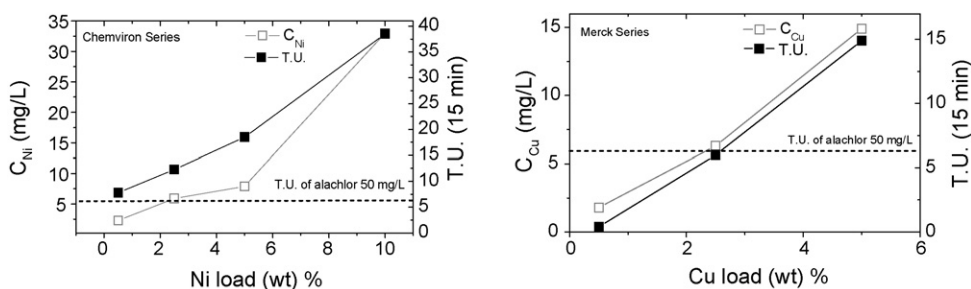


Fig. 6. Influence of catalyst metal load on nickel (left) and copper (right) leaching and ecotoxicity of the effluents (4 h) on stream.

the first 4–6 h. Beyond 8–10 h on stream nickel and copper leaching was much lower and the concentration of metal in the effluent leveled off at values nearly identical independently of the metal load on the catalyst.

Table 5 shows the percentage of metal leached after a time-on-stream of 18 h. In spite of the significant percentage of active phase leached, specially for the catalysts of lower nominal load, it must be pointed out that in all the cases thealachlor conversion maintained a constant value throughout the 18 h time-on-stream as it can be seen in Table 2. However, fairly high values of ecotoxicity were measured in the effluent in spite of the highalachlor conversion achieved (Fig. 6). In most samples the ecotoxicity was even higher than that corresponding to the initialalachlor solution. The ecotoxicity was found to be dependent on the metal load of the catalyst, since it determines the concentration of leached metal. The

Table 5

Metal leaching of the own-made Ni and Cu catalysts (P , 0.24 MPa; τ , 179 kg_{cat} h/mol; Q_G , 100 N mL/min; $H_2:N_2$, 1:1 vol.)

Catalyst	Leaching (%)
Ni	
0.5Ch-Ni	20.0
2.5Ch-Ni	10.4
5Ch-Ni	6.0
10Ch-Ni	8.8
Cu	
0.5Mk-Cu	8.0
2.5Mk-Cu	9.6
5Mk-Cu	7.2
0.5Ch-Cu	12.0
2.5Ch-Cu	7.2
5Ch-Cu	5.1

ecotoxicity of the effluents was especially high for the nickel-based catalysts, and ecotoxicity values as high as 40 T.U. were reached for the effluent treated with the catalyst of highest metal load. The importance of metal leaching on the quality of the treated effluent can be seen from the results obtained with the Pd-based catalysts. In 18 h time-on-stream palladium was not detected in the effluent (technique detection limit < 25 μ g/L) and the ecotoxicity remained at a value of 0.6 T.U., which is consistent with the residual concentration ofalachchlor.

Trying to minimize the metal leaching, the activated carbon supports were subjected to oxidative treatment with nitric acid. This treatment leads to an increase in the amount of oxygen surface groups, as it is well known and in this particular case was reported in a previous work [11]. Two catalysts with a nominal load of nickel and copper of 2.5 wt.% were prepared from the oxidized supports and tested in the hydrodechlorination ofalachchlor for 18 h time-on-stream. The results obtained are summarized in Table 6. Alalachchlor conversion did not show significant differences with respect to the catalysts prepared with the untreated support, although a slight improvement of activity was observed for the Ni-based catalyst. However, the

Table 6

Effect of the oxidative treatment (HNO_3) of the support on the catalytic activity and the ecotoxicity of the effluents (T , 323 K; P , 0.24 MPa; τ , 179 kg_{cat} h/mol; Q_G , 100 N mL/min; $H_2:N_2$, 1:1 vol.)

Catalyst	Conversion (%)	T.U. (15 min)	Leaching (%)
2.5Ch-Ni	81.6	13.3	10.4
2.5ChN-Ni	86.3	1.2	1.6
2.5Ch-Cu	87.2	6.1	7.2
2.5ChN-Cu	87.4	0.7	5.5

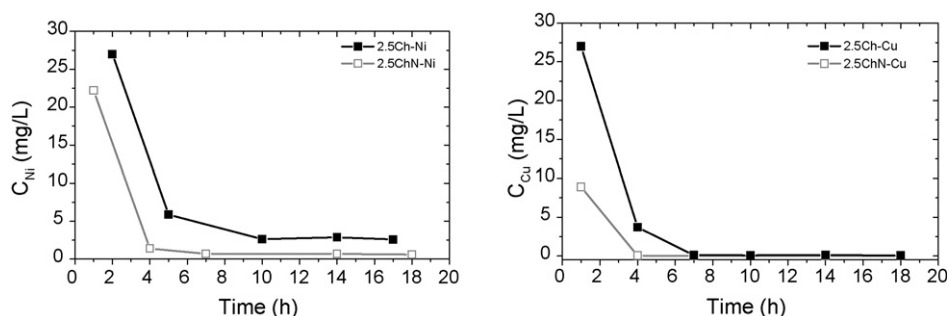


Fig. 7. Comparison of the evolution of nickel (left) and copper (right) leaching with time-on-stream for the catalysts with untreated and treated support.

ecotoxicity was reduced by 90% for the effluents treated with the 2.5ChN-Ni catalyst. This reduction of ecotoxicity can be directly related with the decrease of nickel leaching, which dropped from 7.2 to 1.6% of the initial load. The evolution of nickel concentration with time-on-stream can be seen in Fig. 7. Although in the first 4 h on stream the nickel concentration found in the effluent was high, it can be seen that a further decrease to values much lower than those measured in the case of the catalysts prepared with the untreated support. Therefore, the oxidation of the activated carbon with nitric acid prior to impregnation seems to improve the anchorage of nickel to the support. In the case of the 2.5ChN-Cu catalyst, the reduction of copper leaching was fairly significant during the first 4 h on stream, but after that time the concentration measured in the effluent was equivalent to that obtained for the 2.5Ch-Cu catalyst. Nevertheless, significantly lower values of ecotoxicity were measured for the effluent treated with the 2.5ChN-Cu catalyst, which may indicate the existence of some additional effects, which need further study.

An alternative to minimize the leaching problem would be the catalyst stabilization by accelerated leaching in a preliminary stage, prior to use it in the hydrodechlorination, although the oxidation of the supports can improve other characteristics of the catalyst such as metal dispersion and life time in addition to the control of leaching.

4. Conclusions

The catalytic hydrodechlorination using carbon-supported palladium, copper and nickel catalysts has been studied in order to test its feasibility as a treatment for alachlor bearing waters. High alachlor conversion values and important reductions of ecotoxicity were obtained working under mild conditions of temperature (323–348 K) and pressure (0.24 MPa) with palladium catalysts. Although these palladium on activated carbon catalysts were found as the most active in the hydrodechlorination of alachlor, copper and nickel based catalyst showed also a reasonably good activity, leading to conversion values in the 80–93% range. The main drawback for catalysts based on transition metals was the leaching of the active phase, which caused a detrimental effect on the ecotoxicity of the final effluents. Oxidative treatment of the activated carbon with nitric acid prior to the incorporation of the metallic phase improved the anchorage of copper and nickel

on the activated carbon surface and reduced metal leaching. The minimization of the metal leaching led to a drastic reduction of the ecotoxicity.

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